STUDY OF INTRA-MOLECULAR MOTION OF HYDROXYL GROUP BY PROTON RESONANCE METHOD

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ABSTRACT. The occurrence of molecular or group rotation in crystalline solids has long been a subject of interest and had been investigated by various workers with their different techniques. In the present paper authors have taken a number of organic solids (Alcohols, Quinols and Naphthols) containing hydroxyl group and most of them have been investigated by one of the authors by proton resonance method from rigid lattice temperature to the melting point. It is found that second moment vs temperature curve yielded a discontinuity in the spectrum (but not yet explained) below the transition temperature i.e., before the molecular rotation. This feature in the curve is found in a large number of organic solids which contain OH group, provided OH group is not hindered by the interaction of other heavy substituent groups. The purpose of the present paper is to show that the discontinuity observed in second moment vs temperature curve or the appearance of secondary humps in nuclear magnitude resonance spectra may be due to the intramolecular motion of the hydroxyl group.

It is found that intramolecular rotation of substituent group causes the reduction in the value of rigid lattice second moment and this reduction can be estimated by the equation.

$$<\Delta\omega^2>_{rot} = <\Delta\omega^2>\text{R.L.} \left[\frac{3\cos^2\gamma_{jk} - 1}{2}\right]^2$$

It is shown that reduction in the value of second moment is due to the production of the secondary field at the resonant nucleus. The measurement of spin-lattice relaxation times T_1 carried out at different temperature, demonstrate rotational degree of freedom. From the T_1 measurements the free energy of activation (ΔF_R^*) and enthalpy of activation (ΔH^*) have also been estimated to give support to intra-molecular motion of substituent hydroxyl groups.

INTRODUCTION

Proton magnetic studies of organic solids (Alcohols, Quinols and Naphthols) have been investigated in order to gain information concerning the intra-molecular motion of hydroxyl groups and also about the nature of the motion.

According to simple theory of N.M.R. when an external magnetic field is applied on the sample, it induces a change on a magnetic moment associated with each electron and this change which depends on electronic wave function, is in such a way that it opposes the applied field. The secondary field at any point is also contributed by neighbouring magnetic moment. Therefore, the production of secondary field causes the resonance absorption line to be broadened.

This effect on magnetic resonance absorption line has been interpreted in terms of second moment by Van Vleck (1948). Studies of temperature dependence of second moment (Kambe and Usui (1952), Pryce and Stevens (1950) and by McMillan and Opechowski (1960) show that the conclusion of Van Vleck's work are valid at all temperatures not only very near to absolute Zero. So any effect on nuclear magnetic resonance absorption spectrum can be studied by Van Vleck's theory of second moment. Clough (1963) has also indicated that any motion of an as- sembly of dipolar coupled nuclei has a profound effect on nuclear magnetic resonance spectrum and so also on second moment.

Authors have observed that some organic solids containing hydroxyl group show a remarkable effect on the value of second moment and on resonance spectra with rise of temperature producing secondary humps below the transition temperature. It suggests some sort of motion in the molecule (Andrew, 1950). Since it is evident that molecule itself is not in the motion, hence possibility of intra molecular motion of the substituent group within the molecule cannot be ignored The authors have interpreted the above abnormalities obtained in the values of second moments, in second moment vs temperatures curve of Alcohols, Quinols, and Naphthols, as due to the motion of hydroxyl group, within the molecule.

The intramolecular motion within solids has been also explained with the use of spin-lattice relaxation time T_1. With T_1, the free energy of activation ΔE_R^* and enthalpy of activation ΔH^* have been also estimated in support of intramolecular motion.

THEORY

The motion in molecules or groups in general results from electronic interactions within the sample and from interactions between the externally applied magnetic field and the electrons in the sample (Heinert *et al.* 1959) when an external magnetic field is applied on a sample, each induced electronic magnetic dipole then gives rise to a secondary magnetic field at a nucleus in the direction of the externally applied field and is given by

$$H(\text{secondary}) = <\Delta\mu>(1-3\cos^2\theta_{jk})/r^3{}_{jk}$$

where $<\Delta\mu>$ is the average value of the induced moment, r_{jk} is the length of the vector joining nuclei j and k and θ_{jk} is the angle between vector and applied field axis.

The secondary field is a function of electron distribution in the free volume and of the distance of approach of neighbouring molecules. It is a time varying field and since the time average over all permitted orientations of dipole pair can be less than the steady local field for rigid system. Hence spectrum narrows when rotation sets in.

Alpert (1947, 1949) and Gutowsky and Pake (1950) studied the effect of motion in the lattice using results which were first obtained by Bloembergen *et al.* (1948). Again it has been pointed out by Andrew (1955) that any reduction in the value of second moment with rise of temperature is indicative of some sort of motion in the molecule [either rotational motion as in the case of Benzene (Andrew 1953b) or vibrational motion as in the case Naphthalene (Andrew, 1950)]. The reorientation of solids are recognised by discontinuity observed or by transition curve in second moment vs temperature curve. Hence if any discontinuity is observed, as found but not yet explained, in second moment vs temperature curve ($S-T$ curve) before the molecular rotation or below the transition temperature, it clearly suggests that any sort of intramolecular motion due to the substituent group may be present within the molecule. If such discontinuity in $S-T$ curve is not observed in substituted molecules, it indicates that motion of the concerning substituent group is hindered due to the interactions by other heavy substituent groups present within the molecule.

The effect of the groups or molecular rotation on second moment can be easily estimated. Since the secondary field is a time varying field, hence when the motion in the molecule sets in, the angle θ_{jk} (between applied field and internuclear vector) occurring in the factor $(1-3\cos^2\theta_{jk})$ in the second moment theory of Van Vleck, varies with the time. Since the frequency of rotation are high compared with the frequencies of interest in the resonance, it is time average of $(1-3\cos^2\theta_{jk})$ that effect the second moment.

$$\text{Hence} \quad <(1-3\cos^2\theta_{jk})>\text{ avg} = (1-3\cos^2\theta^1)\,.\,\frac{(3\cos^2\gamma_{jk}-1)}{2}$$

Where γ_{jk} is the angle between radius vector joining j and k and rotation axis. The expression has been solved by Slichter (1963). He found a relation between the second moment at rigid lattice and the rotational second moment and is given by

$$<\Delta\omega^2>_{rot} = <\Delta\omega^2>\text{R.L.}\left(\frac{3\cos^2\gamma_{jk}-1}{2}\right)^2 \qquad \ldots\ (1)$$

where $<\Delta\omega^2>_{rot}$ is rotational second moment and $<\Delta\omega^2>$R.L. is second moment at rigid lattice.

The substituent groups are, however, constrained to their equilibrium position by intramolecular and intermolecular forces. Its motion from one equilibrium position to another is restricted by a potential barrier. The motion may also take place by quantum mechanical tunnelling through the hindering potential barrier. But it is suggested by Newman (1950a) that the process of mechanical tunnelling does not hold good for most of the solid studies.

In the present paper the relaxation phenomenon for the motion of groups in solid molecules have also been discussed. Here only phenomenological description has been taken without adding the details of other theories as transition state

theory (Glasstone *et al.* (1940)) and concept of free volume. If a system transforms an initial state S_1 to a final state S_2 via an activated state S^* ($S_1 \rightleftharpoons S^* \rightleftharpoons S_2$), it requires that the population of S^* should be small compared to S_1 and S_2 where S_1 and S_2 represent orientation of the substituent group in the lattice. This is a restriction which is probably satisfied for molecular motions in solids (Rice, 1958).

The correlation time τ_c for the motion can be written in terms of free activation energy ΔE_R^* which is defined as the difference in the free energy between state S_1 and S^*;

$$\tau_c = \tau_0 \exp\left(\frac{-\Delta E_R^*}{RT}\right)$$

The N. M. R theory developed by B.P.P. which shows a relation between spin lattice relaxation time T_1 and correlation time as

$$T_1 = C\,\tau_c \text{ for } \omega_0 \tau_c << 1$$

Where C is a constant factor and $\omega_0 = 2\pi\nu_0$ where ν_0 is the resonant frequency. The enthalpy of activation ΔH^* can be obtained from the temperature variation of Log T_1 and given by

$$\Delta H^* = \pm(2.303)R\left(\frac{\partial \text{ Log } T_1}{\partial(1/T)}\right) \qquad \ldots (2)$$

where R is the gas constant.

Wilson (1959) has pointed out that the theory of intramolecular rotation in molecules is still unable to account quantitatively for the factor constraining rotation, notably steric effect and properties of electronic structure. Molecular rotation by entire molecule is undoubtedly governed by the same factor, but the theory is even less understood than the theory of intramolecular rotation. There is only fragmentary information to compare the barriers to groups rotation in solids and intramolecular factors contribute strongly to these barriers. The intra-molecular restraints are determined by covalent bonding of molecules and by steric hindrances.

RESULTS AND DISCUSSIONS

Alcohols :

The second moment vs temperature curve for *Pentaerythritol* obtained by Gupta (1963) has been shown in fig. (1). For the determination of second moment for pentaerythritol he has assumed that the positions of hydroxy hydrogens agree with Hvoslef (1958) model and lie exactly in the planes defined by oxygen atoms. The direction of OH bond however deviates by 6° thus making the C-O-H angle about 110°. This feature is very important in determining the position and movement of hydroxy atoms. The portion AB shown in fig. (1) represents the second moment at rigid lattice temperature. After crossing the rigid lattice state an

anomalous shoulder CD has been observed before the transition temperature for OH group rotation and correspondingly there is an appearance of secondary

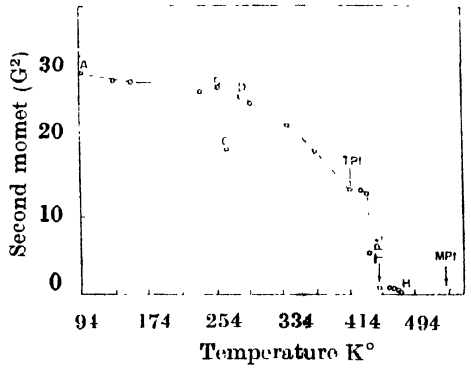

Fig. 1. Second moment versus Temperature curve for pentaerythritol.

hump at room temperature in resonance spectra shown in fig. (2). The possibility of the motion of hydroxy hydrogen has been also indicated by Ellis and Bath (1939) by their infrared studies, Nayer (1938) by his Raman studies and Hvoslef (1958) by his neutron diffraction studies.

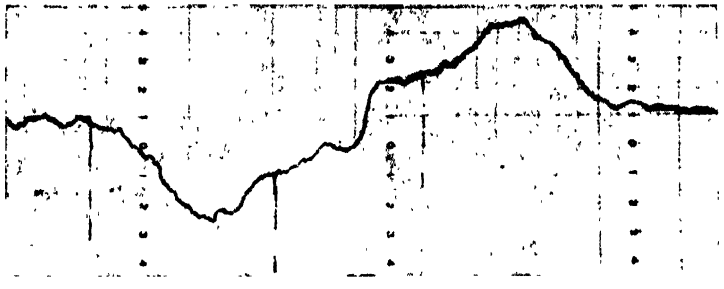

Fig. 2. N.M.R. Spectrum at room temperature showing secondary hump in pentaerythritol.

Eastermann (1929) has observed the dipolement in pentaerythritol and since it is a molecule of the space group ($1\bar{4}$) which cannot have the dipole-moment. Therefore, this dipolemoment is probably due to the intramolecular motion within the solid. Furthermore Sidgwick (1933) and Gilbert and Lansdale (1956) have also observed some sort of intramolecular motion in pentaerythritol molecule.

In pentaerythritol molecule the second moment reduces to 11.8 gauss^2 from its rigid lattice value 28.0 gauss^2. If it is assumed that hydroxyl group is rotating about C-O axis then γ_{jk} the angle of radius vector joining nuclei j and k with the rotation axis, is about 110°. Therefore, according to the equation (1), the value of the second moment should be approximately about 1/2 times of rigid lattice value. In present case the value is reduced from 28.0 gauss^2 to 11.8 gauss^2, approximately the same as required by the theory. The free activation energy ΔE_R^* for the group rotation and enthalpy of activation have been also calculated and given in Table (1).

Similar is the case with *methyl alcohol* cotaining C-O bond as internal rotation axis for hydroxyl group as observed by number of investigators by their Raman and Infrared spectroscopy. N.M.R. study of methyl alcohol (Gutowsky and Pake 1950, and Cook and Drain 1952), also gives approximately similar feature of the resonance spectra as is observed in the case of pentaerythritol. The spectra can be explained on the same lines as authors have discussed for pentaerythritol. Furthermore Muzushima and Kubo (1951) also agree with the present view and estimated the height of the potential barrier arguing that if the over all rotation of the molecule is small as compared with the internal rotation, the barrier height can be estimated from dispersion phenomenon by the use of the absolute reaction theory. He obtained the potential barrier to internal rotation of methyl alcohol from the difference between third law of entropy and molecular entropy.

Such a method has been adopted by Pitzer (1948), Crawford (1940) and Halford (1950). They obtained the potential barrier, for the rotation of the hydroxyl group about C-O axis, approximately about 1000 cal.

In *ethyl alcohol* the motion of the hydroxyl group has been discussed with the experimental thermodynamics quantities by Halford (1949, 1950) and Ito (1952). Gutowsky and Pake (1950) investigated ethylalcohl with N.M.R. method and their results, according to present theory, also give some indication about the motion of the hydroxyl group about C-O bond. The recent work of Barrow (1952) shows that barrier hindering the internal rotation of OH group about C-O axis is about 1000 cal.

Andrew (1950) has investigated *Lauryl alcohol* (n-$C_{10}H_{25}OH$) by proton resonance method and obtained the same discontinuity in ($S-T$) curve before the transition temperature (shown in fig. 3). But the discontinuity observed in spectrum has not been explained by Andrew. This also may be due to the motion of the hydroxyl group about C-O axis present in Lauryl alcohol. The second moment

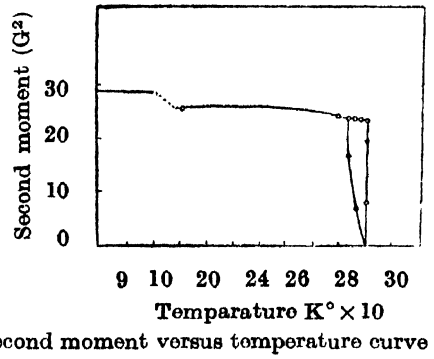

Fig. 3. Second moment versus temperature curve for Lauryl alcohol.

at rigid lattice temperature is found to be 27.77 gauss^2. The rotational second moment is found to be 16.0 gauss^2.

Quinols (Hydroquinones)

The ($S-T$) curve for the *α-Hydroquinone* obtained by Gupta (1963) has been shown in the fig. (4). In which the portion AB represents the second moment at rigid lattice temperature where all the effective motion has been frozen. A discontinuity (C) in the absorption curve has been observed at temperature 325°K. This discontinuity is also observed by Ueberitr *et al.* (1950) in their thermal studies.

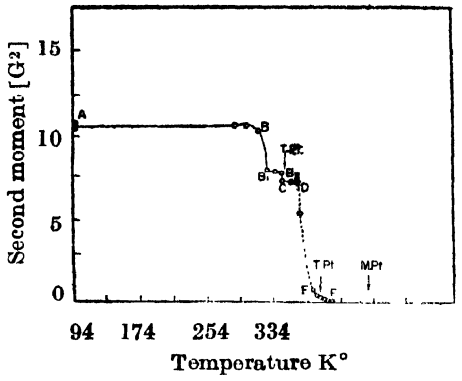

Fig. 4. Second moment versus temperature curve for α-Hydroquinone.

The interpretation of group rotation also receives support from Hidalgo (1950) who found a vibrational frequency shift of OH group in Hydroquinone approximately at about the same temperature. Furthermore high d.c. conductivity has been reported by various workers with other hydrogen bonded structure and is attributed as due to the combined proton transition and dipole rotation (Steam and Erying, 1937).

The value of second moment of α-Hydroquinone at rigid lattice temperature is found to be about 10.7 gauss^2 and before the transition temperature for molecular rotation it reduces almost exactly one quarter of the intramolecular contribution, which satisfies the necessary criterion for rotation (Gutowsky and Pake, 1950).

In *γ-Hydroquinone* (Gupta 1963) the same discontinuity is found in $S-T$ curve (fig. 5). The view of group rotation receives support from Hidalgo (1960)

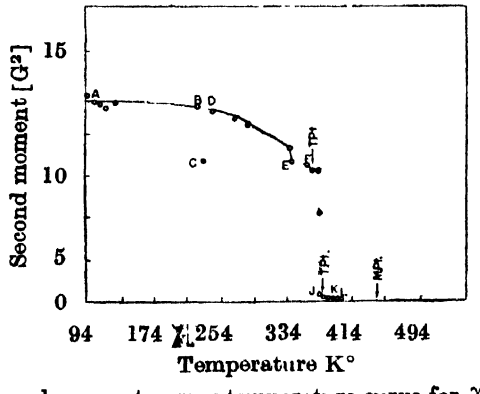

Fig. 5a. Second moment versus temperature curve for γ-Hydroquinone.

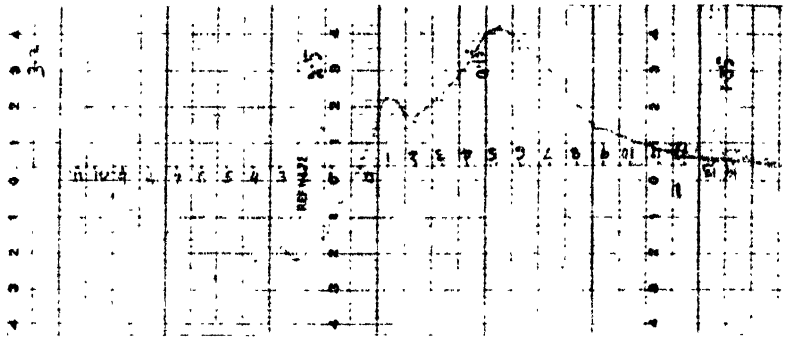

Fig. 5b. N.M.R. spectrum at 285°K showing secondary hump in γ-Hydroquinone.

who observed a vibrational frequency shift of hydroxyl group is Hydroquinone. The second moment at rigid lattice temperature is found to be about 12.0 gauss[2] when intramolecular motion sets in, it reduces to about 1/2 times of rigid lattice value as requirep by theory for rotation about C-O axis.

The spin lattice relation time (T_1) for α and γ-Hydroquinones have also been calculated (Gupta and Agarwal, 1967). With T_1 the value of the free activation energy ΔE_R^* and enthalpy of activation ΔH^* are estimated and given in Table I.

TABLE I

Free activation energy and enthalpy of activation (in K cal/mole)

Compounds	Free activation energy ΔE_R^*	Enthalpy of activation ΔH^*
1. Pentaerythritol	5.27	1 43
2. α Hydroquinone	3.03	3 37
3. γ-Hydroquinone	1.86	1.87
4. α-Napthol	0.51	7.2
5. β-Naphthol	5.9	13.2

Naphthols

In *α-Naphthol* [Gupta, 1967, fig.6] there is some appearance of fine structure at about 312°K. Gupta has attributed this fine structure as due to the vibrational motion of the molecule, arguing that the Naphthol molecule is comparatively large and possesses no symmetry about C-O bond. But it has been pointed out by Andrew (1951) for some organic solids that there is however a decrease in the second moment below the transition temperature. He attributed that this

decrease will be partly due to the rotational oscillation of molecules, but calculation shows that this form of motion is unlikely to account for whole effect.

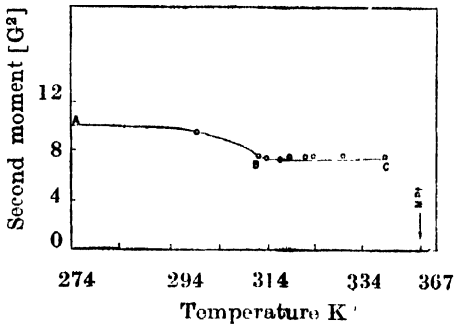

Fig. 6. Second moment versus temperature curve for α-Naphthol.

Andrew stated that it is more likely that the small portion of molecule rotating below the transition point. Therefore, according to the authors views this sort of reduction is due to the motion of hydroxyl group. It gets added support with Nagakura and Gouterman (1957) investigations in which they observed some shift in wave length due to the hydrogen bonding in α-Naphthol. Further more Aihra (1960), with the use of his sublimation pressure method, observed a transition in the crystalline state of α-Naphthol due to some sort of rotation about C-O bond. The rotational second moment is also found to be about 1/2 times of rigid lattice value supporting the theory.

In case of *β-Naphthol* (fig. 7), there appeared a secondary hump in resonance spectrum round about 312°K and some reduction in the value of the second moment in $S-T$ curve. Gupta has attributed this as due to the vibrational motion of the entire molecule. The secondary hump is nearly at the same temperature at which Aihra (1960) observed a transition in the crystalline state due to some sort of rotation about C-O bond. Further more it has been pointed out by Porte *et al.* (1960) for β-Naphthol that OH group forms weak hydrogen bonding with an aromatic nucleus in which the OH bond is directly along the normal to the center

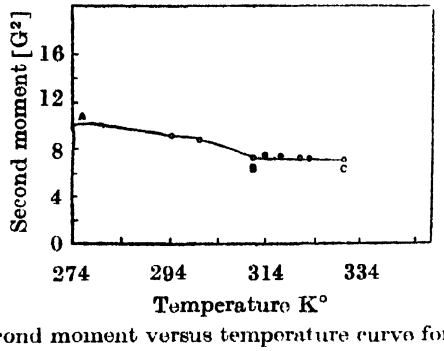

Fig. 7. Second moment versus temperature curve for β-Naphthol.

of aromatic nucleus i.e. there is a tendency for benzene molecule to pack round OH group so that OH bond points along this normal rather than to the side of the

ring. When an external field is applied the current induced in electron system in benzene exerts a secondary field of OH protons and this secondary field opposes the applied field. The result is a shifted proton resonance for OH group in β-Naphthol. Therefore Porte's investigations also suggest about the intramolecular motion of OH group about C-O bond. The value of the rotational second moment is about 1/2 times of the rigid lattice value.

The spin-lattice relaxation times (T_1) for α and β-Naphthols have also been estimated by Agrawal and Gupta (1967) and with which the free activation energy ΔE_R^* and enthalpy of activation have been computed and given in Table 1.

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